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STUDY TO DETERMINE THE FEASIBILITY
OF UTILIZING SKULL-MELTING TECHNIQUES
FOR THE GROWTH OF SINGLE CRYSTALS OF
YTTRIUM VANADATE

FINAL REPORT

JOSEPH F. WENCKUS
WILSON P. MENASHI

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J.F. Wenckus
W.P. Menashi

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The goal of this program is to explore the feasibility of utilizing RF induction heated skull-melting techniques for the growth of optical quality crystals of yttrium vanadate (YVO_4). In a parallel effort, experiments were also carried out to explore the fusion and recrystallization of yttrium aluminum garnet (YAG) in a cold crucible.

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Yttrium vanadate melts were achieved in cold crucibles up to 157 mm in diameter operating at an RF frequency of 3 MHz. However, attempts to Czochralski crystal growth were not successful due to poor thermal geometry and dissociation of the skull-contained melt. Experiments suggest that oxygen overpressures in excess of 2 atmos. may be useful in suppressing the dissociation rate of YVO_4 melts.

Skull-melting of YAG was achieved using an RF frequency of 3 MHz (no melting was observed at lower frequencies). However, the melts tended to slowly de-couple and freeze spontaneously; stable melts could not be maintained for periods beyond 2-3 hours.

TABLE OF CONTENTS

LIST OF REFERENCES

TECHNICAL SUMMARY

Single crystals of yttrium vanadate (YVO_4) offer tantalizing potential for a host of optical applications. However, this potential has not been realized to date due to the many problems encountered in the growth of single crystals with high optical quality.

The congruent melting temperature of YVO_4 is approximately 1825 degrees C. However, at this temperature, YVO_4 exhibits a tendency to dissociate by vaporization of V_2O_5 with the attendant formation of an oxygen-defficient second phase (YVO_3) which has a higher melting point (~1925 degrees C) and limited solubility in YVO_4. This dissociation can be controlled to some extent, by providing oxygen over-pressure surrounding the YVO_4 melt. However, the iridium crucibles typically used to contain the melt are readily oxidized under these conditions and the sublimation product (IrO_2) contaminates the melt and resultant crystal.

The goal of this program is to explore the feasibility of utilizing RF induction heated skull-melting techniques for the growth of optical quality crystals of YVO_4. In a parallel effort, experiments were also carried out to explore the fusion and recrystallization of yttrium aluminum garnet (YAG) in a cold crucible.

While we succeeded in melting YVO_4 using skull-melting procedures, attempts at crystal growth were not successful due to poor thermal geometry in the skull-contained melt. Lack of control of crystal diameter, coupled with spontaneous freezing of the melt surface, could not be overcome using cold crucibles up to 157 mm diameter operating at RF frequencies up to 3 MHz. Dissocation of the contained melt persisted at oxygen over-pressures up to 2 atmos. However, the results suggest that higher pressures of oxygen may suppress the loss of V_2O_5 from the contained melt and higher RF frequencies might be used to provide a radial melt temperature gradient more appropriate for Czochralski crystal growth.

Skull-melting of yttrium aluminum qarnet was achieved using an RF frequency of 3 MHz (no melting was observed at 250 Khz). However, the melts tended to decouple slowly and stable melts could not be sustained over the extended periods required for controlled crystal growth. Regardless of the applied RF power, spontaneous freezing occurred within 2-3 hours.

I INTRODUCTION:

Single crystal yttrium vanadate (YVO_4) is attractive as a potential laser host. When doped with neodymium (Nd) and pumped along the a-axis, the stimulated emission cross section is about five times that of Nd:YAG. Such a laser rod should have a lower oscillation threshold and be useful for both CW and pulsed operation where minimum total energy input is desired.

Undoped single crystal YVO_4 also shows promise as a superior substitute for calcite as a polarizer material. YVO_4 is a positive, uniaxial crystal with a birefringence of +0.226, approximately 25% higher than the value of -0.172 for calcite. The refractive index of YVO_4 is higher than that of calcite across the usable spectrum and shows values of 1.958 and 2.168 at 1.06 microns. Moreover, the refractive index of YVO_4 remains relatively constant with temperature up to 300 degrees K.

The useful transmission range of YVO_4 extends to 5 microns which makes polarizers possible in the important 2 to 5 micron range in laser systems.

With a hardness of 450 KHN, YVO_4 is equivalent in hardness to that of frequently used glass compositions. This suggests that surface finishing to optical quality should be relatively straight forward.

Clearly, single crystal YVO_4 offers tantalizing potential for a host of optical applications. However, this potential has not been realized due to the many problems encountered in the reproducable growth of high optical quality single crystals of YVO_4.

The equilibrium phase diagram for the Y_2O_3 - V_2O_5 system indicates that YVO_4 melts congruently at 1825 degrees C. Iridium crucibles have been used for the Czochralski growth of YVO_4 crystals; however, this container must be heated in an inert atmosphere or very low O_2 pressure, to prevent rapid iridium oxidation with the consequent contamination of the contained melt. Unfortunately, under these operating conditions, there is the attendant difficulty of preventing, or at the very least controlling, the vaporization loss of V_2O_5 and the formation of an oxygen-defficient second phase of YVO_4 (YVO_3) which exhibits a slightly higher melting point (~100 degrees C) and limited solubility in molten YVO_4.

The need for oxygen in the ambient atmosphere above the contained YVO_4 melt has been reported earlier by several researchers, thus in a practical sense, eliminating the use of traditional containers such as iridium crucibles for the Czochralski growth of YVO_4 crystals. This need has prompted the exploration of containerless methods such as the skull-melting technique for this application.

With the skull-melting technique, refractory oxides are melted by direct, high-frequency induction heating in a water-cooled, segmented copper cold-crucible assembly. The melt is effectively contained by a sintered shell (or "skull") of the contained oxide which remains in contact with and physically supported by, the walls of the cold crucible. Since the melt is contained by a sintered shell of its own composition, the possibility of contamination by the crucible is eliminated. Of equal importance, in the case of YVO_4 melt-containment, the water-cooled skull-melting assembly can be used to contain melts at extreme temperatures (well in excess of 2500 degrees C) under oxidizing atmospheres.

This report reviews the application of present-day skull-melting technology to the growth of single crystal YVO_4, the problems which were encountered, and the results achieved.

II. BACKGROUND INFORMATION

A. YTTRIUM VANADATE (YVO_4) CRYSTAL GROWTH

Yttrium vanadate (YVO_4) is a tetragonal single crystal with unit cell dimensions of $\underline{a}$=7.123 and $\underline{c}$=6.191. Structurally, it is similar to zircon, $ZrSiO_4$, which also possesses a unique arrangement with highly anisotropic properties. The principle feature of the structure [1] in YVO_4 are chains of alternating edge-sharing VO_4 tetrahedra and YO_8 triangular dodecahedra. These are undoubtedly responsible for the growth habit, cleavage, extreme birefringence, thermal conductivity, expansion differences and many crystal growth anomolies.

The space group of YVO_4 is D_{4h} I_4/amd with four (4) formula units per cell; the density is approximately 4.3 gm/cc and the hardness is between three (3) to five (5) on the Mohs scale. Phase diagrams of the vanadium-oxygen and Y_2O_3 - V_2O_5 systems are shown in Figures 1 and 2.

Single crystals of YVO_4 have been grown via the flux [2], flame-fusion (Verneuil) [3], floating-zone [4], Czochralski [5] and sealed-crucible Bridgman [6] techniques. While crystals of the best quality have been grown via the Czochralski method, the resultant crystals were far from perfect; typically, the crystals were darkly colored and contained inclusions, bubbles and cleavage fractures.

The inclusions found in YVO_4 crystals have severely restricted their optical applications due to light scattering. These inclusions include randomly-scattered impurity dendrites, iridium platelets, as well as bubbles or dendrites which are characteristic of constitutional supercooling. The dendrites have been characterized by Morrison [5] as composed of segregated impurities, random stringers, structure-controlled stringers and sporadic helices.

The high melting temperature of stoichiometric YVO_4 (~1825 degrees C) dictated the use of iridium crucibles for Czochralski growth experiments. However, at elevated temperatures, YVO_4 loses oxygen rapidly resulting in compositional changes and the vaporization loss of V_2O_5. The work by Ropp [7] confirms that under the usual Czochralski crystal growth conditions, YVO_4 should be treated as a multi-component rather than a mono-component system.

In order to reduce the problem of V_2O_5 vaporization from the YVO_4 melt, it is evident that an external gas (oxygen) over pressure is required to maintain melt stoichiometry. Unfortunately, the iridium crucibles oxidize and sublime quite rapidly when used under oxidizing ambients; thus cold-crucible (skull-melting) methods were considered as a potentially attractive alternative for melt containment to explore the Czochralski growth of YVO_4 crystals.

B. SKULL MELTING TECHNOLOGY

Basically, the skull-melting process as applied to the growth of refractory oxide crystals, involves the direct high frequency induction heating of the oxide mixture contained in a water-cooled crucible-like structure which is commonly referred to as a cold crucible. The melt formed is contained by a sintered shell (or "skull") of identical composition so that the problems of crucible reaction and containment of even the most refractory melts have been virtually eliminated.

At room temperature, most oxides and oxide mixtures are highly insulating and essentially transparent to the RF field. It is necessary therefore, to preheat oxide charge to a temperature at which it becomes sufficiently conductive so that it can be coupled directly by the RF field. This is typically accomplished by placing metallic chips of the constituent oxide within the charge contained in the cold crucible. At room temperature, the RF field (typically at 3-5 MHz) couples to and heats the metallic chips. In turn, the glowing metal chips heat the adjacent surrounding oxide powder and when the localized region of the oxide charge is heated to approximately 1200 - 1500 degrees C, the oxide becomes sufficiently conductive to permit direct coupling with the RF field. The metallic chips are quickly oxidized during fusion and are effectively dissolved in the resultant melt. Graphite plates are also used as a pre-heat element; if the skull-melting operation is carried out under oxidizing conditions, the combustion products of high-purity graphite (CO_2 and CO) do not contaminate the resultant melt.

The skull-melting techniques as applied to the growth of single crystal cubic zirconia have been described by Nassau [9] and Aleksandrov, et aI [10]. An extensive bibliography of cold crucible designs and applications is presented in a report by Wenckus and Menashi [11].

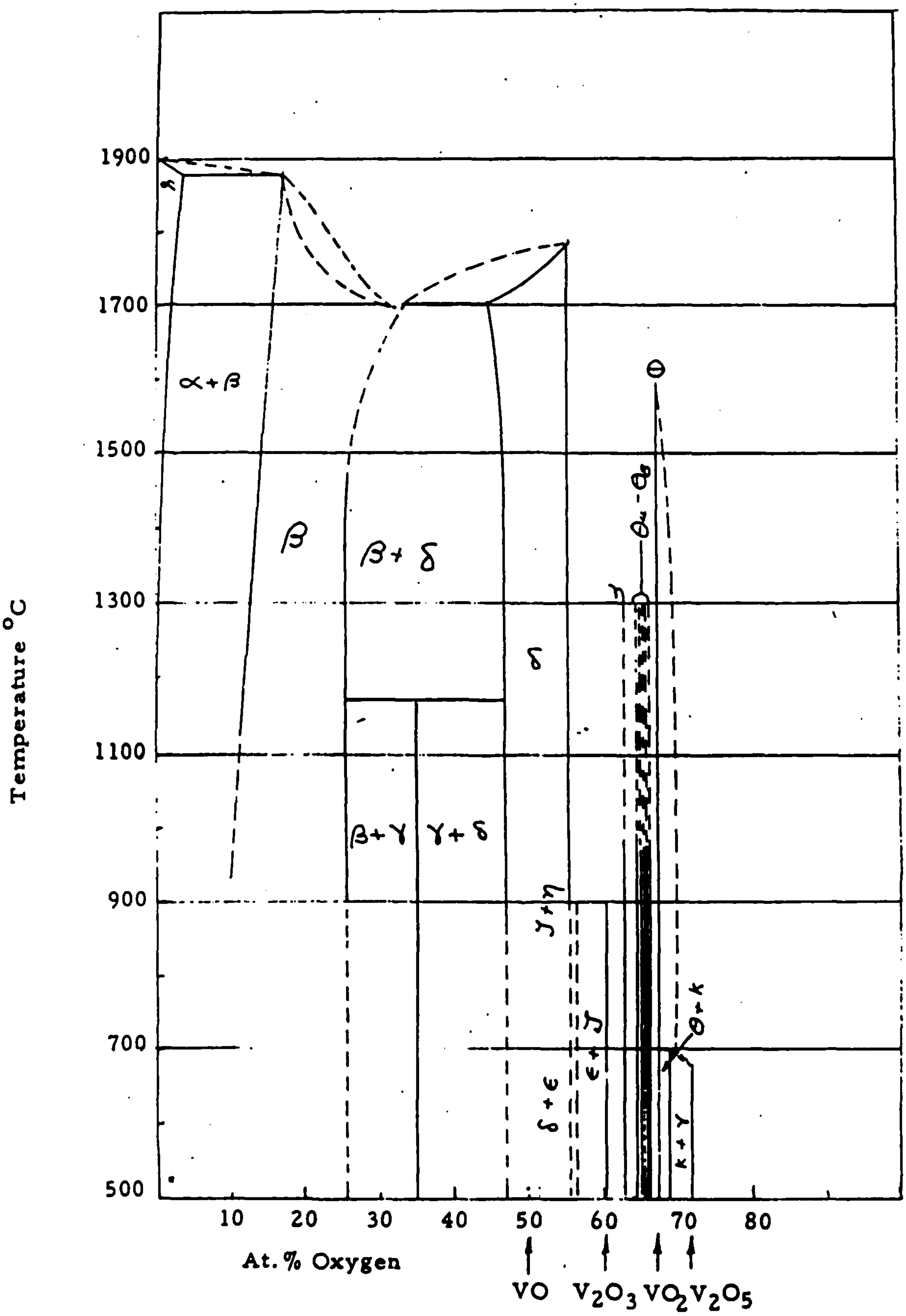

FIGURE 1. THE VANADIUM-OXYGEN SYSTEM

REF. W. ROSTOKER - THE METALLURGY OF VANADIUM - WILEY

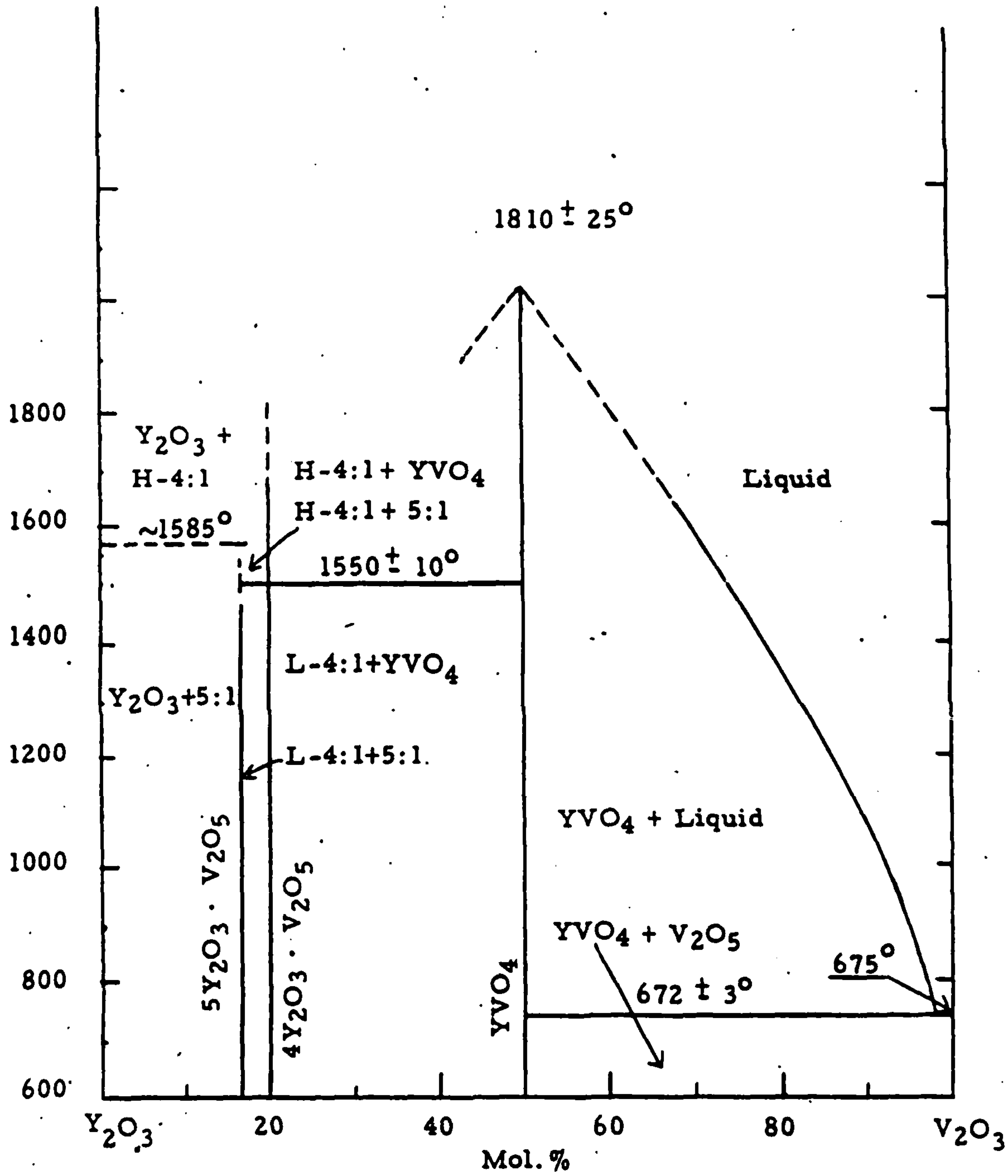

FIGURE 2. PHASE DIAGRAM-SYSTEM Y_2O_3-V_2O_5

E.M. LEVIN, J. AM. CERAM. SOC., 50 [7] 381 (1967)

III EXPERIMENTAL RESULTS

The objective of the program is to determine the feasibility of utilizing skull melting techniques for the growth of optical quality single crystals of yttrium vanadate (YVO_4). In parallel with this effort, experiments were also carried out to explore the fusion and recrystallization of yttrium aluminum garnet (YAG).

A. APPARATUS AND EXPERIMENTAL PROCEDURES USED

During the course of this program, skull-melting experiments were carried out in water-cooled cold-crucible assemblies designed and constructed by Ceres Corporation. Initial experiments were carried out in a 73mm I.D. cold crucible assembly illustrated in Figure 3. A larger cold-crucible (approx. 157 mm I.D.) with essentially the same configuration, was also employed to explore the effects of skull diameter on radial thermal gradients within the contained melt.

All Skull-melting experiments were carried out using a 50kW output RF generator having dual-frequency capability, ie, nominal output frequencies of 250 kHz and 3-5 MHz could be utilized interchangeably.

Initially, the skull-melting experiments were carried out in air. Rapid, and often violent decomposition of YVO_4 melts in air prompted the installation of the cold-crucible assembly into a controlled-atmosphere chamber shown in Figure 4. The water-cooled stainless steel chamber (approximately 275 mm I.D.) fitted with a large rectangular viewing port (150 mm x 275 mm) in the access door, is capable of operating at pressures ranging from 10^{-2} torr to 2.0 atmospheres. The top of the chamber is fitted with a crystal withdrawal mechanism designed to operate at withdrawal rates ranging from 0.01 mm to 20 mm/hour with a total stroke of 20 cm. Simultaneous crystal rotation at controlled rates up to 50 RPM, is also provided.

The cold crucible assembly mounted with the controlled atmosphere chamber is shown in Figure 5. Typically, a 4-turn, water-cooled copper RF coil was used for the fusion experiments. It was necessary to design and construct a low-loss RF feed-through assembly to introduce the high frequency (3-5 MHz) power into the chamber; the feed through was designed to operate under oxidizing conditions at pressures up to 5 atmos. (approximately 73 psig).

Figure 5 also shows the boron nitride seed holder assembly which utilizes a short section stainless steel ball chain to insure vertical seed alignment. An alumina ceramic gas inlet tube is positioned adjacent to the cold crucible.

The larger cold-crucible assembly (157 mm I.D.), mounted in a controlled atmosphere chamber, was also employed during the course of the program to explore the effects of melt diameter on the radial thermal gradients of the contained melt.

The feed material was prepared by V-blending stoichiometric quantities of Y_2O_3 (4-9's MCI Megon) with V_2O_5 (3-9's Union Carbide Corporation) or in the case of the YAG experiments, Al_2O_3 (4-9's Adolf Meller Co.).

The cold crucible assembly was filled with mixed powder along with a small quantity (~10 gms) of yttrium metal. At room temperature, the RF energy first coupled into the yttrium metal chips which were heated rapidly. The incandescent yttrium metal chips caused localized heating of the powdered charge until the oxide mixture was sufficiently heated to become conductive in order to initiate RF coupling and fusion.

Upon melting, the yttrium metal chips were fully oxidized and dissolved into the resulting oxide melt. Alternatively, small high-purity graphite discs (1" diam x 1/8" thick) were used in place of the yttrium metal chips to pre-heat the oxide charge. The graphite disc could be removed or allowed to burn and vaporize completely with no apparent contamination of the molten oxide.

Typically, the YVO_4 and YAG powder mixtures fuzed quite rapidly and complete melts (approximately 1.5 kg in weight) could be achieved within 20-30 minutes after start-up time.

B. RESULTS OBTAINED

$\underline{YVO_4}$

A total of ninety-two (92) YVO_4 skull-melting experiments were carried out using a variety of operating conditions in an effort to establish stable melt conditions for the growth of optical quality crystals. The operating variables explored and the results achieved are summarized below:

Ambient Atmosphere

Initial YVO_4 skull-melting experiments were carried out in air. The powder mixture melted very rapidly accompanied by violent bubbling and spattering of the melt. In air, the melts continued to out-gas (smoke) and bubble throughout the typical 2-hour holding period.

Attempts to lower the YVO_4 charge slowly (@ 0.3cm/hour) out of the RF field in order to produce spontaneously-nucleated YVO_4 crystals via directional-recrystallization proved to be unsuccessful. The melts appeared to decouple and quench quite rapidly resulting in a solidified mass comprised of small, black, bubble-filled grains.

An open-top quartz sleeve was then placed around the skull-melting assembly in an effort to explore the use of oxygen-and nitrogen-enriched atmospheres over the exposed YVO_4 melt. While melt bubbling and outgassing appeared to be somewhat reduced, in all cases the melt surface remained sufficiently active to prevent controlled crystal growth.

In an effort to control the ambient atmosphere surrounding the YVO_4 melt, the skull-melting assembly was then installed in the furnace chamber shown in Figures 4 and 5. YVO_4 melting experiments carried out under a flowing N_2 atmosphere (30 CFH at 1 atmos) provided relatively calm, stable melts which could be maintained for extended periods. The use of flowing O_2 under the same conditions (30 CFH at 1 atmos) resulted in violent melt-bubbling and out-gassing. Flowing nitrogen-oxygen gas mixtures were also explored and stable, relatively quiet melts could only be maintained when the O_2 content in the mixture did not exceed 1% by volume (at a pressure of 2 atmos).

Atmospheres of pure O_2 above the YVO_4 melt were investigated at pressures up to 2 atmos (~30 psiq). The maximum pressure limitation was due primarily to the rectangular configuration of the large viewing port located in the access door of the furnace chamber. In fact, during the course of a YVO_4 fusion experiment carried out under an O_2 over-pressure of 2.3 atmos, the rectangular viewing port cracked and we were forced to terminate the experiment prematurely.

The YVO_4 melts appeared to be more stable with increasing O_2 over-pressure. However, at 2 atmos of O_2 we were still not able to reduce the activity of the melt surface sufficiently to permit controlled CZochralski crystal growth.

RF Frequency

In an effort to investigate the effects of RF frequency on the fusion and stability of YVO_4 melts, a series of experiments were carried out using RF frequencies of 250 KHz and 3.5 MHz. In all cases, YVO_4 fusion and melting could be readily achieved. However, at the lower RF frequency (250 KHz), it proved to be far more difficult to maintain a stable melt, i.e., the melt exhibited a stronger tendency to decouple and freeze uncontrollably regardless of the level of RF power applied.

While we can conclude that the higher RF frequency appears to be necessary to insure the maintenance of a stable YVO_4 melt in the smaller cold-crucible assemblies, it may well be that the lower frequency (with its greater RF skin depth penetration) would prove to be advantageous for larger diameter melts (greater than 200 mm).

Crystal Growing Experiments

As noted above, a total of ninety-two (92) YVO_4 fusion/crystal growing experiments were carried out. Figure 6 shows a molybdenum wire "seed" rod positioned above the YVO_4 melt (under a N_2 atmosphere). Note that the molten pool (which is approximately 12 mm deep) is surrounded by a sintered YVO_4 shell which is contained within the water-cooled copper cold-crucible assembly.

Figure 7 shows the early stage of YVO_4 crystal pulling experiment carried out under a N_2 atmosphere. The initial polycrystalline section (approximately 6-7 mm in diameter) appears to be transparent while the flared section of the growing ingot is opaque, black and oxygen-defficient. Figure 8 shows a polycrystalline YVO_4 section (approximately 5 mm diam) in contact with the melt as viewed at 10 x magnification. Note that the fluid flow pattern on the surface is not as uniform as that observed in oxide melts contained in the more commonly used hot-wall crucibles.

Virtually all of the YVO_4 crystal growing experiments carried out in the smaller cold-crucible assembly (73 mm I.D.) resulted in opaque, black, polycrstalline ingots. Subsequent annealing of these O_2-defficient ingots in air at 1200 degrees C resulted in powdering and disintergration accompanied by a marked color change (black to yellow-green).

We also noted that radial melt temperature gradient in the small cold-crucible assembly was very flat, quite unlike the gradient typically observed when using the traditional, hot-wall crucibles. Despite attempts to modify the gradient by using a directed gas jet(s) at the center of the melt or conical radiation shielding, it proved to be extremely difficult to initiate controlled Czochralski crystal growth and, if initiated, virtually impossible to reduce melt temperature to enlarge the growing crystal without spontaneous flaring and surface freezing initiated at the walls of the cold crucible. It became obvious that the radial penetration was equal to, or greater than, the radius of the melt contained in the small cold crucible. This factor, combined with the rapid melt stirring due to RF field effects produced a relatively uniform radial melt temperature which effectively prevented controlled Czochralski crystal growth.

Based upon these results, subsequent attempts at YVO_4 crystal growth were carried out using a larger (157 mm I.D.) cold-crucible assembly. Since the RF penetration depth into the contained melt is dependant primarily on the RF frequency, it was hoped that the radial thermal gradients in the larger diameter melt might be more suitable for controlled crystal growth.

A series of eighteen (18) crystal growth runs were carried out in this large cold-crucible (melt weight approx 6 Kg each) using high frequency (3 MHz) RF power. While the radial temperature gradients in the melt showed some improvement, as the melt temperature was lowered to increase the diameter of the growing crystal, it was not possible to prevent uncontrolled rapid flaring of the growing ingot and spontaneous freezing of the melt. Small polycrystalline ingots of YVO_4 were produced during the course of these experiments. The individual grains were transparent, straw-yellow in color, interspersed with inclusions and cracks.

YAG

In parallel with the work relating to the skull-melting and crystal growth of YVO_4, twenty-two (22) experiments were also carried out on the fusion and recrystallization of yttrium aluminum garnet (YAG).

The procedures and apparatus used for these experiments were identical to those described for YVO_4. All YAG melting/recrystallization experiments were carried out in air. Initial attempts to skull melt YAG at low frequencies ($\tilde{}$250 KHz) proved to be unsuccessful i.e., no melting was achieved regardless of the RF power applied. YAG fusion was achieved quite rapidly at higher RF frequencies (~3.5 MHz) and relatively stable melts (with persistent out-gassing) could be maintained for extended periods of time (3-6 hours). It is worth noting however, that the RF power to the skull-contained melt had to be increased continuously to prevent spontaneous decoupling.

Attempts at YAG crystal growth by directional recrystallization of the melts were carried out by slowly lowering the melt from the RF field at a rate of 2 mm/hour. The melts tended to decouple quite rapidly as the lowering operation proceeded and it was not possible to maintain a stable melt for the extended periods of their required for controlled directional recrystallization.

Upon examination of the solidified YAG melts, we found very small YAG or $YAlO_3$ + Al_2O_3 crystals similar to those reported by Czlavsky and Viechnicki(12) in their experiments on the unseeded Bridgman growth of Nd:YAG crystals.

Due to the instability of the induction-heated YAG melt, no attempts were made to grow YAG crystals via the Czochralski technique from skull-contained results.

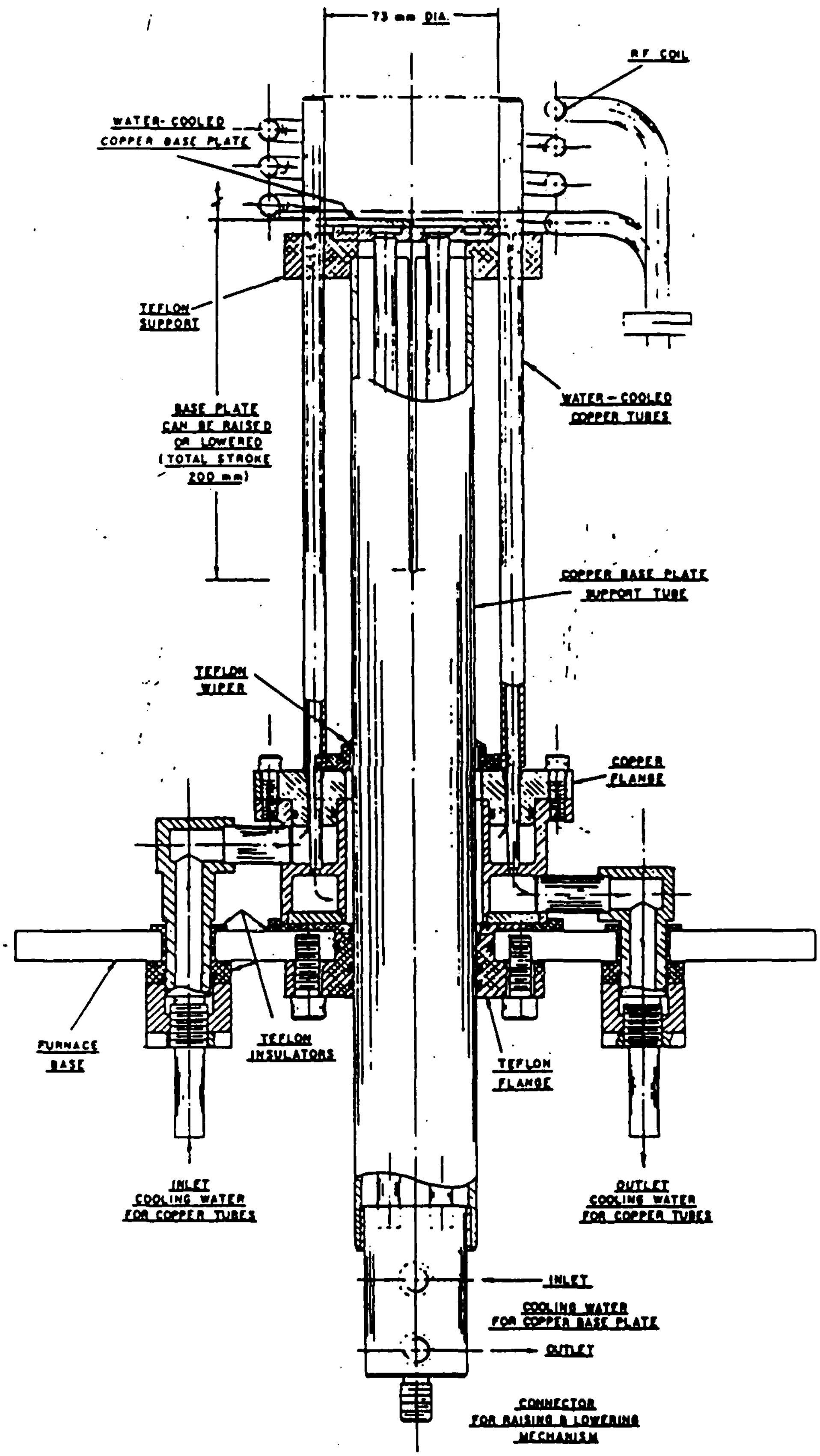

FIGURE 3. WATER COOLED COLD CRUCIBLE ASSEMBLY

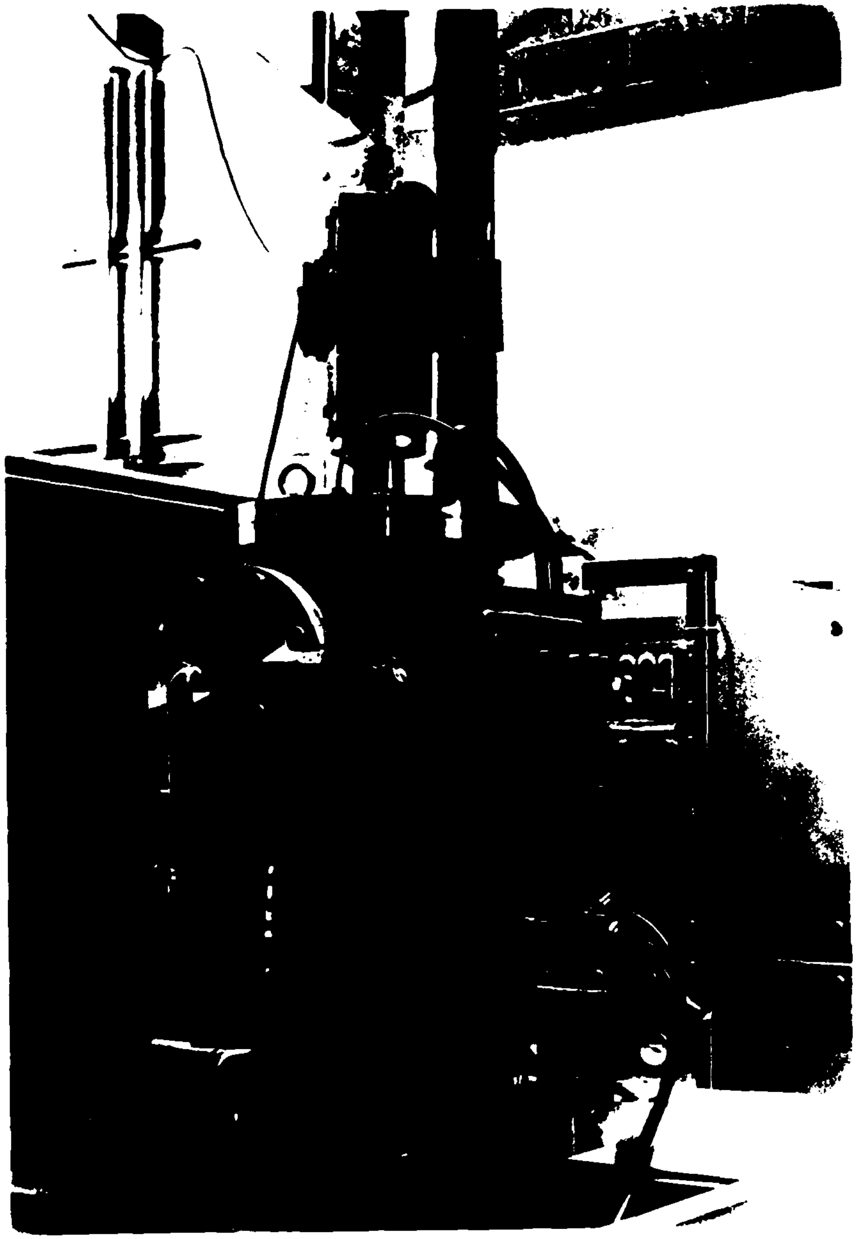

FIGURE 4. CRYSTAL GROWING FURNACE CHAMBER

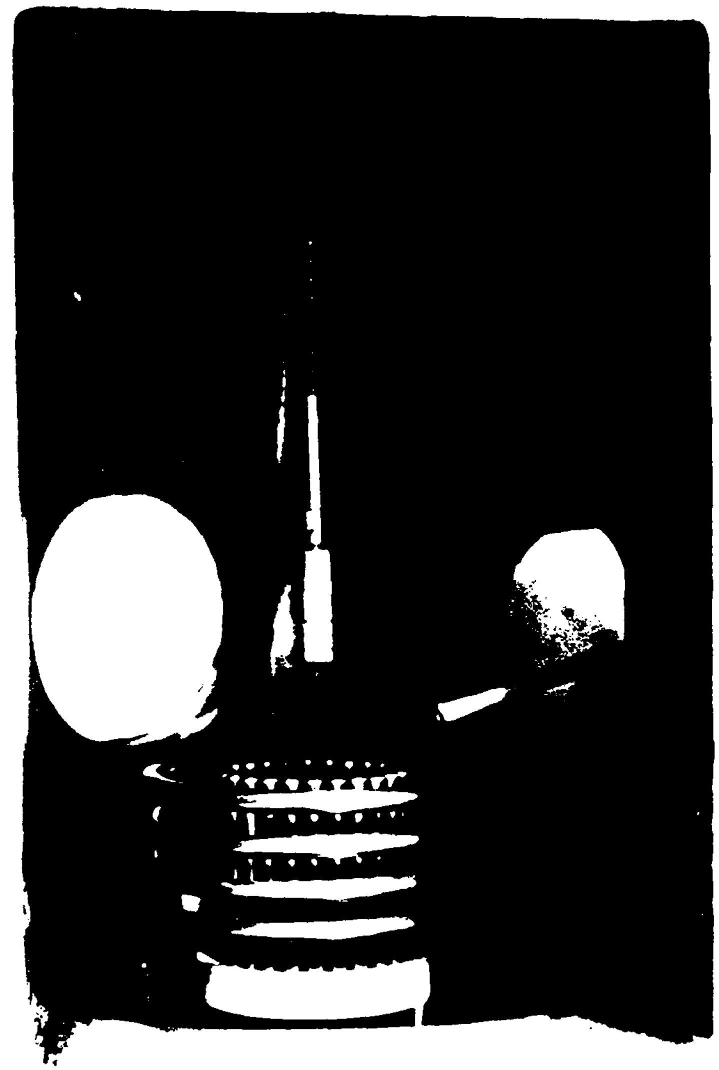

FIGURE 5. COLD CRUCIBLE ASSEMBLY MOUNTED IN THE FURNACE CHAMBER

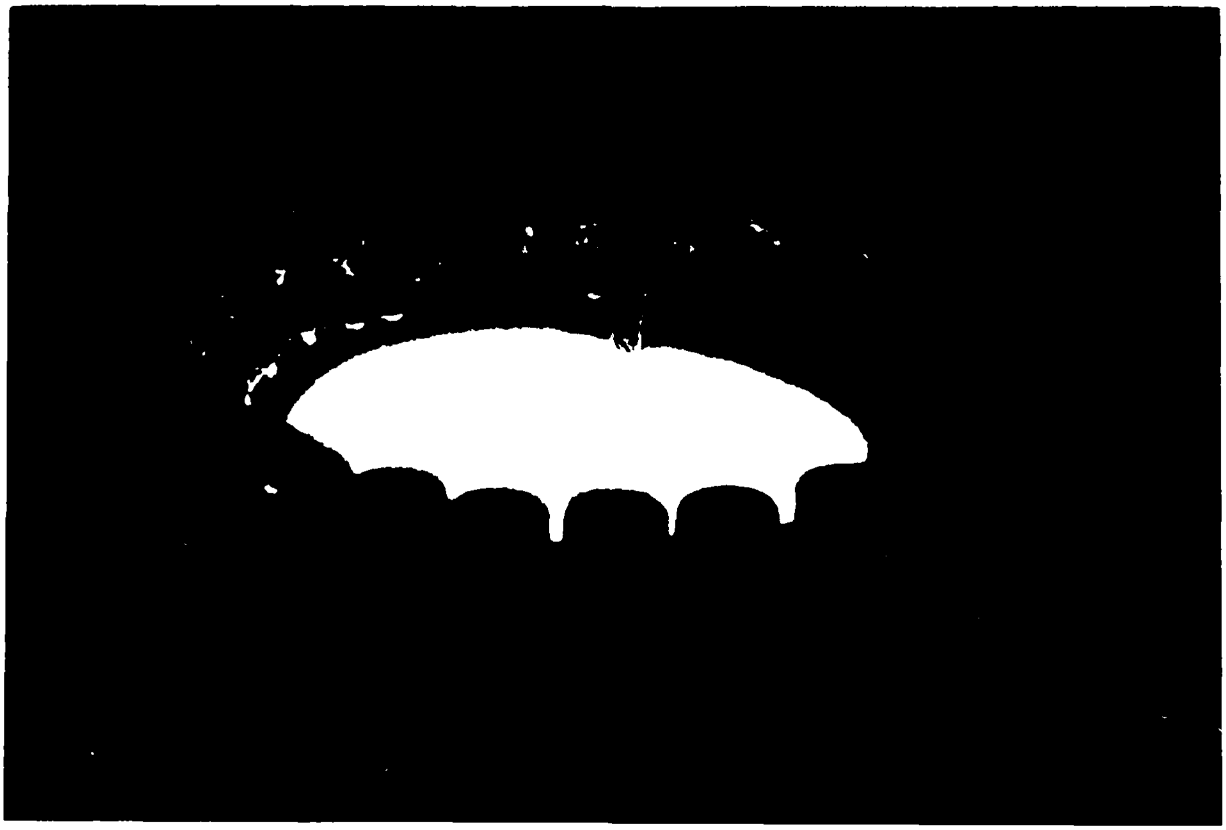

FIGURE 6. MOLYBDENUM SEED ROD POSITIONED ABOVE THE YVO_4 MELT

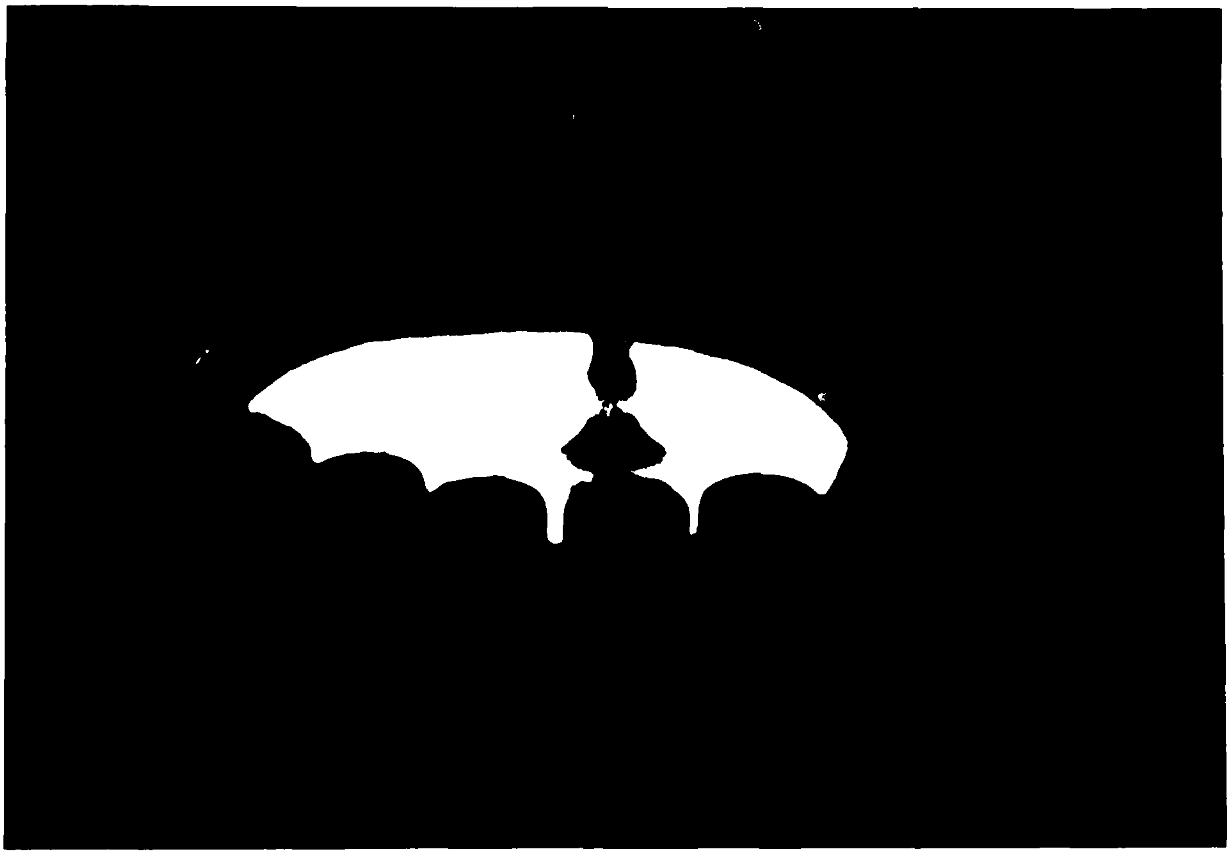

FIGURE 7. YVO_4 CRYSTAL PULLING EXPERIMENT

FIGURE 8. POLYCRYSTALLINE YVO_4 INGOT (APPROX DIAM 5 MM) IN CONTACT WITH THE MELT CONTAINED IN A COLD CRUCIBLE

IV DISCUSSION AND RECOMMENDATIONS

While we did not succeed in producing single crystals of yttrium vanadate (YVO_4) or yttrium aluminum garnet (YAG) using skull-melting techniques, we can offer the following observations:

A.) YVO_4 can be melted and contained in an RF-coupled cold crucible. However, it appears to be necessary to provide oxygen-over pressures (in excess of 2 atmos) to prevent continuous dissociation of the contained melt under skull-melting conditions.

B.) Due to the penetration depth of the RF field into the YVO_4 melt, either higher RF frequencies (greater than 3 MHz) or alternatively, significantly larger melt diameters (greater than 157 mm) should be employed to provide a radial melt temperature gradient more suitable for Czochralski crystal growth. Enlargement of crystal diameter during growth and spontaneous freezing of the melt surface proved to be extremely difficult to control using the present cold crucible systems at the available RF frequencies (250 Khz and 3 MHz).

Knowledge of the electrical conductivity is a prerequisite for any analysis of the optimum frequency required to maintain stable oxide melts in an RF-coupled cold crucible. Unfortunately, the available data on refractory oxide melts is meager, and where it exists, not too reliable. There appears to be no high temperature data available for YVO_4.

C.) Melting of yttrium aluminum garnet (YAG) could be achieved using high frequency (3 MHz) skull-melting techniques; however, melt stability proved to be an insurmountable problem. The melts tended to slowly de-couple and freeze spontaneously after 3-4 hours of operation. Use of higher RF frequencies (above 5 MHz) may provide stable melts with longer retention time.

It is interesting to note that pure Al_2O_3 melts exhibit the same behavior when contained in a cold crucible and Russian workers have reported that spontaneous de-coupling and freezing can be reduced by the use of very high frequency RF power (~15 MHz).

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